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(11) Publication number:

**0 391 415 B1**

(12)

## EUROPEAN PATENT SPECIFICATION

- (49) Date of publication of patent specification: **29.03.95** (51) Int. Cl.<sup>6</sup>: **C07F 9/6561**, C09B 47/067,  
C09B 47/073, C07F 9/40,  
(21) Application number: **90106541.7** C07F 9/53, G11B 7/24,  
C07D 487/22  
(22) Date of filing: **05.04.90**

(54) **Naphthalocyanine compounds and production thereof.**

(30) Priority: **06.04.89 JP 87230/89**

(43) Date of publication of application:  
**10.10.90 Bulletin 90/41**

(45) Publication of the grant of the patent:  
**29.03.95 Bulletin 95/13**

(84) Designated Contracting States:  
**CH DE FR GB IT LI**

(56) References cited:  
**EP-A- 0 296 876**  
**FR-A- 2 187 988**  
**US-A- 2 613 129**

**RESEARCH DISCLOSURE. no. 163, November**  
**1977, HAVANT GB pages 78 - 79; ANONY-**  
**MOUS: 'Phthalocyanine dyestuffs containing**  
**phosphonic acid groups '**

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## Description

The present invention relates to naphthalocyanine compounds, intermediates therefor and a process for producing them. More particularly, it relates to novel naphthalocyanine compounds which strongly absorb light of near infrared region and which are chemically stable and highly soluble in an organic solvent.

Naphthalocyanine compounds which are known as dyestuffs absorbing near infrared light are stable to light and heat, and have excellent fastness.

The dyestuffs which absorb near infrared light known to the art are, for example, cyanines, phthalocyanines, dithionickel complexes, naphthoquinones, anthraquinones, indophenols and azo compounds. The dyestuffs are applicable to optical disks, compact disks, laser printers, laser reading, electrophotographic photosensitive members and infrared cut filters for semiconductor light receptors.

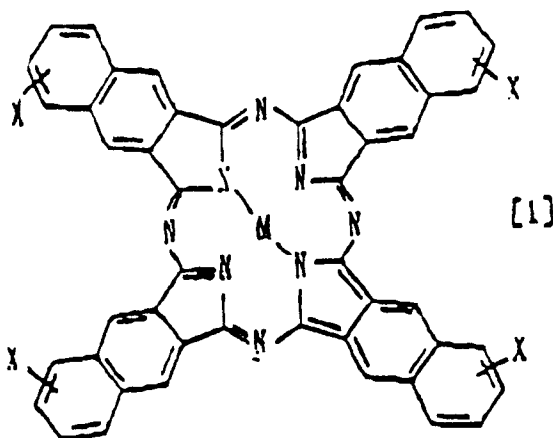
It is also proposed in JP-A-25886/1986, 163891/1986, 233287/1987, 72594/1988, 122788/1987, 39388/1988, 252344/1985 and 16891/1986 that the dyestuffs can be employed in the recording layer of the optical disk.

A dyestuff for a DRAW type optical recording medium is required to have strong absorption in the region of a laser oscillation, high reflectance, high stability and forming abilities of a uniform recording medium layer.

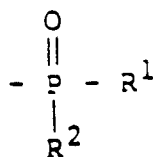
However, the cyanine dyestuffs are poor in color fastness to light, and therefore a recording medium using the cyanine dyestuffs is insufficient in stability. The phthalocyanine or naphthalocyanine dyestuffs are poor in solubility to a polar solvent, and therefore form an uneven recording medium layer. In order to improve the solubility of naphthalocyanine dyestuffs, US-A-4,492,750 and JP-A-215662/1986 disclose a naphthalene ring substituted with an alkyl group, substituted silyl group, alkoxy group, phenoxy group or aralkoxy group. JP-A-72761/1988 and 95269/1988 disclose compounds in which the central metal is substituted with an alkoxy group or alkylsiloxy group. The proposed naphthalocyanine dyestuffs however, damage guide digs on a substrate and are still insufficient in solubility to alcohols.

It is the object of the present invention to provide novel naphthalocyanine compounds which strongly absorb light of the near infrared region and which are chemically stable and highly soluble in an organic solvent.

This object is achieved by the naphthalocyanine compound of the invention represented by the following formula [1];



wherein X represents



(wherein R<sup>1</sup> and R<sup>2</sup> respectively represent a hydroxyl group, an alkyl group, an aryl group or an alkoxy group) and M represents 2H, a metal atom, a metal oxide residue or a metal chloride residue.

The present invention also provides a process for producing the above mentioned naphthalocyanine compounds.

Also, the present invention provides intermediates suitable for producing the naphthalocyanine compound of the present invention.

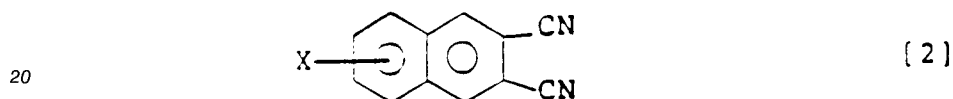
5 Further, the present invention provides a process for producing the above mentioned intermediates.

In the formula [1], examples of the substituents X are  $-P(=O)(C_6H_5)_2$ ,  $-P(=O)(OC_2H_5)_2$ ,  $-P(=O)(C_{10}H_{21})_2$  and  $-P(=O)(OH)_2$ . The substituent X may be located at any of the 5, 6, 7 and 8 positions of the naphthalene ring. In the definition of  $R^1$  and  $R^2$  the alkyl group may have 1 to 18, preferably 6 to 12 carbon atoms. The aryl group may have 6 to 12 carbon atoms with a phenyl or naphthyl group which may be substituted by a lower ( $C_{1-4}$ ) alkyl group being preferred. The alkoxy group may have 1 to 10, preferably 1 to 4 carbon atoms.

In the formula (1), the symbol M represents 2H, a metal atom, a metal oxide residue or a metal chloride residue. Examples of the metal atoms are Cu, Zn, Ni, Co, Fe, Ge, Sn, Pb, Ti, Cr, Mn, Al and In. Examples of the metal oxide residues are  $\text{>Ti=O}$ ,  $\text{>V=O}$  and  $\text{>Sn=O}$ .

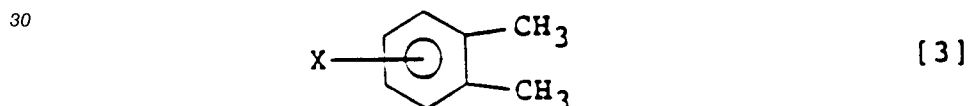
15 Examples of the metal chloride residues are  $\text{>SiCl}_2$ ,  $\text{>GeCl}_2$ ,  $\text{>AlCl}$ ,  $\text{>SnCl}_2$  and  $\text{>InCl}$ .

The 2,3-dicyanonaphthalene [2] having a substituent X which is represented by

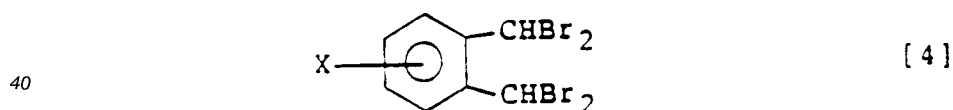


wherein X is the same as mentioned above, is an intermediate for producing the naphthalocyanine compounds of the present invention. The substituent X may be located at either 5 or 6 position of the naphthalene ring.

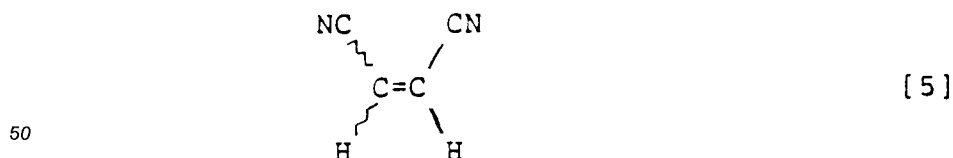
25 The intermediate can be prepared by reacting 3- or 4-bromo-o-xylene with a phosphine oxide or a phosphite in the presence of a catalyst to form a X substituted-o-xylene represented by formula [3]



35 wherein X is the same as mentioned above, reacting it with N-bromosuccinimide to form a compound represented by formula [4]



wherein X is the same as mentioned above, and then reacting the compound [4] with fumaronitrile represented by formula [5]



Examples of the phosphine oxides are chlorodiethyl phosphine oxide and chlorodiphenyl phosphine oxide.

55 Examples of the phosphites are methyl phosphite, ethyl phosphite and decyl phosphite. The catalyst includes anhydrous nickel chloride. The amount of the phosphine oxide is 1.0 to 1.1 mol based on 1 mol of 3- or 4-bromo-o-xylene. The amount of the phosphite is 1.1 to 1.2 mol based on 1 mol of 3- or 4-bromo-o-xylene. The catalyst can be used in an amount of 0.05 to 0.2 mol based on the 1 mol of 3- or 4-bromo-o-

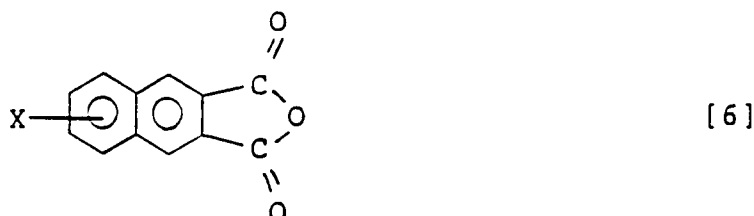
xylene.

The amount of N-bromosuccinimide is 4.0 to 4.5 mol based on 1 mol of the X substituted-o-xylene. The amount of fumaronitrile is 1.0 to 1.3 mol based on 1 mol of the compound [4].

The naphthalocyanine compound [1] wherein M represents 2H, may be prepared by reacting the intermediate [2] in an alcohol in the presence of a proton transferring accelerator. In the reaction, the proton transferring accelerator includes 1,8-diazabicyclo[5,4,0]undec-7-ene and 1,5-diazabicyclo[4,3,0]-5-nonen. The accelerator may be present in an amount of more than stoichiometric amount based on 1 mol of the intermediate. Examples of the alcohols are n-butanol, n-amyl alcohol, 2-methoxyethyl alcohol and 2-ethoxyethyl alcohol. The amount of the alcohol is not limited, but preferably used in an amount of 500 to 2,000 ml, preferably about 1,000 ml. The obtained naphthalocyanine compound wherein M is 2H and R<sup>1</sup> and R<sup>2</sup> respectively represent an alkoxy group, i.e. tetrakis(dialkoxyphosphoryl) naphthalocyanine, may be hydrolyzed with e.g. hydrochloric acid to form the naphthalocyanine compound [1] wherein M is 2H and R<sup>1</sup> = R<sup>2</sup> = OH.

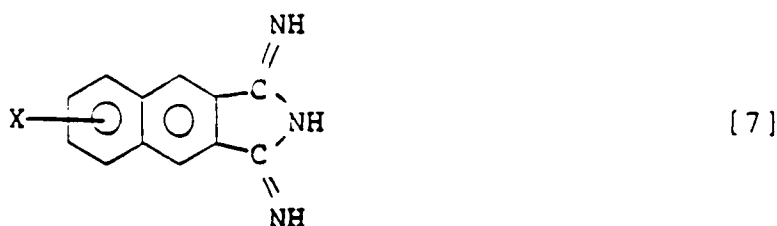
The naphthalocyanine compound [1] wherein M represents a metal atom, a metal oxide residue or a metal chloride residue, may be prepared by reacting the intermediate [2] with a metal, a metal oxide or a metal chloride under molten conditions or in a high boiling point solvent. Examples of the metals are Cu, Zn, Ni, Co, Fe, Ge, Sn, Pb, Ti, Cr, Mn, Al and In. Examples of the metal chlorides are CuCl, Cu<sub>2</sub>Cl<sub>2</sub>, SnCl<sub>2</sub>, InCl<sub>3</sub>·4H<sub>2</sub>O, AlCl<sub>3</sub>, TiCl<sub>4</sub>, SiCl<sub>4</sub>, GeCl<sub>2</sub>, FeCl<sub>3</sub> and SnCl<sub>4</sub>. Examples of the metal oxides are PbO<sub>2</sub> and PbO. Examples of the high boiling point solvents are solvents which have a boiling point of more than 180 °C, for example, trichlorobenzene (b.p. 218-219 °C), quinoline (b.p. 238 °C), chloronaphthalene (b.p. 263 °C) and bromonaphthalene (b.p. 289 °C). The amount of the metal, metal oxide and metal chloride in the reaction process is 0.25 to 2 mol, preferably 0.3 to 0.4 mol based on 1 mol of the intermediate [2]. The amount of the high boiling point solvent is not limited and can be varied by a reaction scale and the like. In the above process, the reaction may be carried out in molten conditions in which the reactants are melted at a temperature of 180 to 220 °C for 3 to 6 hours.

Another process for preparing the naphthalocyanine compound [1] wherein M represents a metal atom, metal oxide residue or metal chloride residue, comprises reacting a X substituted naphthalene-2,3-dicarboxylic anhydride represented by formula [6]



wherein X is the same as mentioned above, with the metal, the metal oxide or the metal chloride under molten conditions or in a high boiling point solvent in the presence of urea and an optional catalyst. Examples of the catalysts are ammonium molybdate, ammonium vanadate, ammonium arsenate and ammonium phosphate. The other reactants are the same as mentioned above. In the reaction, the amounts of the reactants are 5 to 10 mol for urea, 0.25 or more (preferably 0.3 or more) for the metal, metal oxide or metal chloride and 1,000 to 1,500 ml for the high boiling point solvent, based on 1 mol of the compound [6].

The naphthalocyanine compound [1] wherein M represents a metal atom, a metal oxide residue or a metal chloride residue, may be obtained reacting a X substituted 1,3 diiminobenz (f) isoindoline represented by formula [7]



wherein X is the same as mentioned above,  
 with the metal, the metal oxide or the metal chloride under molten conditions or in a high boiling point solvent in the presence of a tertiary amine. Examples of the tertiary amines are trimethylamine, triethylamine, tri-n-butylamine, triethanolamine and tri-n-butanolamine. The other reactants are the same as mentioned above. In the reaction, the amounts of the reactants are 0.25 to 2 mol (preferably 0.3 to 0.4 mol for the metal, metal oxide or metal chloride, a catalyst amount for the tertiary amine and 100 to 2,000 ml (preferably 500 to 1,000 ml) for the high boiling point solvent.

The naphthalocyanine compounds of the present invention are highly soluble in organic solvents including polar solvents, such as alcohols, ketones, ethers, esters, aliphatic halogenated hydrocarbons and aromatic hydrocarbons. They therefore can be easily coated by spraying, rolling, dipping and spinning to form a uniform coating layer without dissolving the substrate. They also absorb the light of the near infrared region especially 780 to 830 nm which is used for AlGaAs semiconductor laser. The compounds are very stable to light, heat, acid and alkali. Other special features of the naphthalocyanine compounds are that the absorption characteristics of an electric spectrum are changed by a sort of an organic solvent. For example, tetrakis(diphenylphosphoryl) naphthalocyanine has an absorption characteristics as shown in Fig.8 in chloroform, but it is changed to the chart of Fig.18 in tetrahydrofuran.

Fig.1 shows an NMR spectrum of the compound of Example 1.

Fig.2 shows an NMR spectrum of the compound of Example 2.

Fig.3 shows an NMR spectrum of the compound of Example 3.

Fig.4 shows an NMR spectrum of the compound of Example 4.

Fig.5 shows an IR spectrum of the compound of Example 4.

Fig.6 shows an NMR spectrum of the compound of Example 5.

Fig.7 shows an IR spectrum of the compound of Example 5.

Fig.8 shows an electron spectrum of the compound of Example 6.

Fig.9 shows an IR spectrum of the compound of Example 6.

Fig.10 shows an electron spectrum of the compound of Example 7.

Fig.11 shows an IR spectrum of the compound of Example 7.

Fig.12 shows an electron spectrum of the compound of Example 8.

Fig.13 shows an IR spectrum of the compound of Example 8.

Fig.14 shows an electron spectrum of the compound of Example 9.

Fig.15 shows an IR spectrum of the compound of Example 9.

Fig.16 shows an electron spectrum of the compound of Example 10.

Fig.17 shows an IR spectrum of the compound of Example 10.

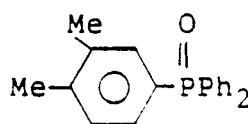
Fig.18 shows an electron spectrum of the compound of Example 6.

The present invention is illustrated by the following Examples which, however, are not construed as limiting the present invention to their details.

#### Example 1

##### Preparation of 4-diphenylphosphoryl-o-xylene

A reaction vessel was charged with 100 ml of tetrahydrofuran (THF) which had been dried with lithium aluminum hydride, to which 2.83 g (0.1209 mol) of magnesium turnings was added. With refluxing, a dried THF solution of 19.6 g (0.106 mol) of 4-bromo-o-xylene was added dropwise over one hour. After the completion of the addition, it was refluxed for about one hour and then cooled to 5 to 10 °C at which a dried THF solution of 25 g (0.106 mol) of chlorodiphenylphosphine oxide was added dropwise over about 3 hours. After the completion of the addition, it was mixed at 50 to 60 °C for 2 hours and allowed to stand for cooling. Then, 100 ml of dilute hydrochloric acid and 100 ml of diethyl ether were added to the resultant solution and mixed for 30 minutes. It was then extracted three times with 200 ml of diethyl ether. The extracted solution was rinsed three times with a 5 % sodium hydrogencarbonate solution and dried with anhydrous sodium sulfate. The ether solution was condensed and subjected to column chromatography to obtain 25 g of white solid which had a chart (Fig.1) of NMR spectrum in CDCl<sub>3</sub> to find the following chemical structure;

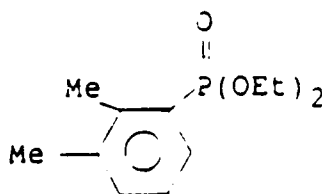


$\delta$ Value    7.45 (13H, br)  
               2.23 (6H, br-s)

## 10 Example 2

### Preparation of 3-diethoxyphosphoryl-o-xylene

15 A mixture solution of 25.0 g (0.135 mol) of 3-bromo-o-xylene and 2.0 g (0.015 mol) of anhydrous nickel chloride was heated to 150 to 160 °C, to which 26.9 g (0.162 mol) of triethyl phosphate was added for 1 to 2 hours. After the completion of the addition, it was mixed at that temperature and then cooled. To the cooled solution, 30 ml of water was added and mixed for another 30 minutes. It was then extracted three
 20 time with 100 ml of diethyl ether. The extracted solution was rinsed three times with a 5 % sodium hydrogencarbonate solution and dried with anhydrous sodium sulfate. The ether solution was condensed and subjected to column chromatography to obtain 20 g of transparent liquid which had a chart (Fig.2) of NMR spectrum in CDCl<sub>3</sub> to find the following chemical structure;

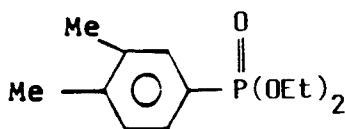


30  $\delta$  Value    7.92 - 7.13 (3H, m)  
               4.13 (4H, d.q.,  $J_{H-H} = J_{H-P} = 7.26$  Hz)  
               2.50 (3H, s)  
               2.30 (3H, s)  
 35              1.33 (6H, t,  $J_{H-H} = 7.26$  Hz)

## Example 3

### Preparation of 4-diethoxyphosphoryl-o-xylene

40 Transparent liquid of 20.8 g was obtained as generally described in Example 2, with the exception that 4-bromo-o-xylene was employed instead of 3-bromo-o-xylene. It had a chart (Fig.3) of NMR spectrum in CDCl<sub>3</sub> to find the following chemical structure;



50  $\delta$  Value    7.66 - 7.28 (3H, m)  
               4.11 (4H, d.q.,  $J_{H-H} = J_{H-P} = 7.04$  Hz)  
               2.30 (6H, s)  
 55              1.32 (6H, t,  $J_{H-H} = 7.04$  Hz)

## Example 4

## Preparation of 6-diphenylphosphoryl-2,3-dicyano naphthalene

A reaction vessel was charged with 100 ml of carbon tetrachloride in which 10.3 g (0.035 mol) of 4-diphenylphosphoryl-o-xylene and 25.3 g (0.142 mol) of N-bromosuccinimide were dissolved. Then, 0.3 g of benzoyl peroxide was added and irradiated by a mercury lamp with refluxing for 10 to 12 hours. After cooling, the precipitated white solid was filtered off and the filtrate was condensed under reduced pressure. The obtained solid was rinsed with a small amount of methanol, and then dried to obtain 21.3 g of 1,2-bis-(dibromomethyl)-4-diphenylphosphoryl benzene. Its analysis showed as follow;

(1)

Elemental analysis		
Calculated value (%)	C; 38.61,	H; 2.41
Measured value (%)	C; 37.97,	H; 2.39

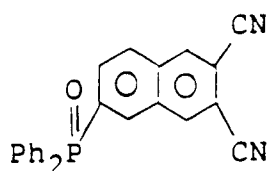
(2) NMR spectrum in  $\text{CDCl}_3$  $\delta$  Value 8.28 - 7.39 (13H, m)

7.26 (1H, s)

7.06 (1H, s)

Next, 21.3 (0.034 mol) of the obtained 1,2-bis(dibromomethyl) 4 diphenylphosphoryl benzene and 3.5 g (0.045 mol) of fumaronitrile were dissolved in 100 ml of anhydrous N,N-dimethylformamide, to which 23.2 g (0.155 mol) of sodium iodide was added with stirring and mixed at about 75 °C in a nitrogen atmosphere for another 5 hours. After finishing the reaction, the reaction solution was poured in about 500 ml of ice and water and mixed for about 50 minutes. Sodium hydrogensulfite was added thereto until the solution turned to light yellow, and then mixed for about one hour. The precipitated light yellow solid was filtered out and rinsed with water. The solid was dried under reduced pressure to obtain crude solid of 8.5 g.

The crude solid of 7.0 g was recrystallized from ethanol to obtain white crystal of 5.85 g. The crystal was identified as 6-diphenylphosphoryl-2,3-dicyano naphthalene by the following analysis;



(1)

Elemental analysis			
Calculated value (%)	C; 76.19,	H; 3.97,	N; 7.41
Measured value (%)	C; 75.53,	H; 4.11,	N; 7.45

(2) NMR spectrum in  $\text{CDCl}_3$  (Fig.4) $\delta$  Value 8.46 - 7.41 (15H, m)(3) IR spectrum (thin layer method of  $\text{CHCl}_3$  solution) (Fig.5)2,200  $\text{cm}^{-1}$  (an absorption derived from  $\text{C}\equiv\text{N}$ )1,210  $\text{cm}^{-1}$ , 1,175  $\text{cm}^{-1}$  (an absorption derived from  $\text{Ph}_2\text{P}=\text{O}$ )

## Example 5

## Preparation of 6-diethoxyphosphoryl-2,3-dicyano naphthalene

A reaction vessel was charged with 500 ml of carbon tetrachloride in which 47.7 g (0.197 mol) of 4-diethoxyphosphoryl-o-xylene and 144 g (0.809 mol) of N-bromosuccinimide were dissolved. Then, 1.0 g of benzoyl peroxide was added and irradiated by a mercury lamp with refluxing for 10 to 12 hours. After cooling, the precipitated white solid was filtered off and the filtrate was condensed under reduced pressure. The obtained viscous liquid was mixed with a small amount of an ether and subjected to an ultrasonic to precipitate solid. The solid was filtered to obtain 40 g of white solid. The solid was identified as 1,2-bis-(dibromomethyl)-4-diethoxyphosphoryl benzene by the following analysis;

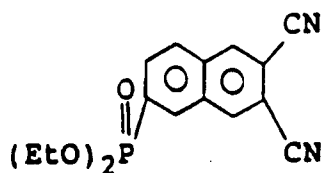
(1)

Elemental analysis		
Calculated value (%)	C; 27.82,	H; 2.90
Measured value (%)	C; 26.25,	H; 2.68

(2) NMR spectrum in  $\text{CDCl}_3$ 

$\delta$  Value 8.12 - 7.76 (3H, m)  
 7.23 (1H, s)  
 7.07 (1H, s)  
 4.17 (4H, d.q.,  $J_{\text{H-H}} = J_{\text{H-P}} = 7.26$  Hz)  
 1.36 (6H, t,  $J_{\text{H-H}} = 7.26$  Hz)

Next, 20.0 (0.036 mol) of the obtained 1,2-bis(dibromomethyl)-4-diethoxyphosphoryl benzene and 3.5 g (0.045 mol) of fumaronitrile were dissolved in 100 ml of N,N-dimethylformamide, to which 23.2 g (0.155 mol) of sodium iodide was added with stirring and mixed at about 75 °C in a nitrogen atmosphere for another 5 hours. After finishing the reaction, the reaction solution was slowly poured into 2,000 ml of a 5 % sulfurous acid solution to produce white slurry. After the completion of pouring, salt was precipitated with sodium chloride and filtered out and rinsed with water. The solid was dried under reduced pressure to obtain solid of 5.1 g. The solid was identified as 6-diethoxyphosphoryl-2,3-dicyano naphthalene by the following analysis;



(1)

Elemental analysis			
Calculated value (%)	C; 61.15,	H; 4.78,	N; 8.92
Measured value (%)	C; 60.09,	H; 4.76,	N; 8.89

(2) NMR spectrum in  $\text{CDCl}_3$  (Fig.6)

$\delta$  Value 8.61 (1H, s)  
 8.45 (1H, s)  
 8.41 (1H, s)  
 8.12 (1H, s)  
 8.04 (1H, s)  
 4.19 (4H, d.q.,  $J_{\text{H-H}} = J_{\text{H-P}} = 7.04$  Hz)  
 1.36 (6H, t,  $J_{\text{H-H}} = 7.04$  Hz)



- (3) IR spectrum (thin layer method of  $\text{CHCl}_3$  solution) (Fig.7)  
 2,250  $\text{cm}^{-1}$  (an absorption derived from  $\text{C}\equiv\text{N}$ )  
 1,290  $\text{cm}^{-1}$ , 1,260  $\text{cm}^{-1}$  (an absorption derived from  $(\text{C}_2\text{H}_5\text{O})_2\text{P}=\text{O}$ )

#### 5 Example 6

##### Preparation of tetrakis(diphenylphosphoryl)-naphthalocyanine

A mixture of 1.124 g (3 mmol) of 6-diphenylphosphoryl-2,3-dicyanonaphthalene and 3 ml of dried amyl  
 10 alcohol was heated to reflux in a nitrogen atmosphere, to which 0.5 ml (3.3 mmol) of 1,8-diazabicyclo[5,4,0]-  
 unde-7-cene was added dropwise for about 15 minutes. It was mixed with refluxing for about 10 hours, and  
 then cooled to about 70 °C. After adding 30 ml of methanol to the mixture, it was mixed for one hour. Dark  
 green solid was precipitated and filtered, followed by rinsing with methanol. The solid was then dispersed in  
 300 ml methanol and heated to reflux for about one hour. It was filtered under vacuum at an elevated  
 15 temperature and rinsed with methanol until filtrated methanol was transparent. The obtained dark green  
 solid was dried under reduced pressure to obtain 600 mg of solid. The solid was identified as tetrakis-  
 (diphenylphosphoryl)naphthalocyanine by the following analysis;

(1)

20

Elemental analysis			
Calculated value (%)	C; 76.09,	H; 4.10,	N; 7.40
Measured value (%)	C; 72.80,	H; 4.33,	N; 7.23

25

(2) Electron spectrum in  $\text{CHCl}_3$  (Fig.8)

Electron spectrum in THF (Fig.18)

(3) IR spectrum (KBr method) (Fig.9)

#### 30 Example 7

##### Preparation of tetrakis(diethoxyphosphoryl)naphthalocyanine

A reaction was conducted with 1.2 g (4.7 mmol) of 6-diethoxyphosphoryl-2,3-dicyanonaphthalene, 3 ml  
 35 of dried amyl alcohol and 0.8 ml (5.3 mmol) of 1,8-diazabicyclo[5,4,0]unde-7-cene as generally described in  
 Example 6. After the completion of the reaction, 5 ml of water and 5 ml of methanol were added and mixed,  
 and salted out with sodium chloride. The obtained solid was filtered and rinsed with water. It was rinsed with  
 a mixture of 3/7 of methanol/water until filtrate was transparent. The obtained dark green solid was dried  
 under reduced pressure to obtain 450 mg of solid. The solid was identified as tetrakis(diethoxyphosphoryl)-  
 naphthalocyanine by the following analysis;

40

(1)

45

Elemental analysis			
Calculated value (%)	C; 61.05,	H; 4.93,	N; 8.90
Measured value (%)	C; 60.92,	H; 4.90,	N; 8.87

(2) Electron spectrum in  $\text{CHCl}_3$  (Fig.10)

(3) IR spectrum (KBr method) (Fig.11)

50

#### Example 8

##### Preparation of tetrakis(dihydroxyphosphoryl)naphthalocyanine

A mixture of 100 mg of tetrakis(diethoxyphosphoryl)naphthalocyanine and 100 ml of a 10 % hydrochloro-  
 55 ric acid was heated to reflux for about 5 hours and then allowed to cool to obtain dark green solid. The  
 obtained solid was rinsed with about 50 ml of methanol and dried under reduced pressure to obtain about  
 55 mg of solid. The solid was identified as tetrakis(dihydroxyphosphoryl)naphthalocyanine by the following

analysis;

(1)

5

Elemental analysis			
Calculated value (%)	C; 55.71,	H; 2.90,	N; 10.53
Measured value (%)	C; 55.50,	H; 2.87,	N; 10.75

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(2) Electron spectrum in 5 % sodium hydrogencarbonate solution (Fig.12)

(3) IR spectrum (KBr method) (Fig.13)

Example 9

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Preparation of tetrakis(diphenylphosphoryl)vanadynaphthalocyanine

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A mixture of 1.0 g of 6-diphenylphosphoryl-2,3-dicyanonaphthalene, 0.3 g (1.33 mmol) of vanadium chloride, 0.5 ml of tri-n-butylamine and 3 ml of alpha-bromonaphthalene was mixed at 180 to 200 °C for about 3 hours and then allowed to cool to 60 °C. Next, 50 ml of methanol was added and mixed for one hour to precipitate dark green solid. The solid was rinsed with methanol until filtrate was transparent. It was then dispersed in 300 ml of a 3 % hydrochloric acid and mixed at 70 to 80 °C for about one hour. After filtering, it was rinsed with water and then rinsed with 300 ml of methanol. The obtained dark green solid was dried under reduced pressure to obtain 525 mg of solid. The solid was identified as tetrakis-(diphenylphosphoryl)vanadynaphthalocyanine by the following analysis;

25

(1)

Elemental analysis			
Calculated value (%)	C; 73.00,	H; 3.80,	N; 7.09
Measured value (%)	C; 70.13,	H; 4.02,	N; 6.84

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(2) Electron spectrum in  $\text{CHCl}_3$  (Fig.14)

(3) IR spectrum (KBr method) (Fig.15)

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Example 10Preparation of tetrakis(diphenylphosphoryl)chloroindiumnaphthalocyanine

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A mixture of 1.5 g (4 mmol) of 6-diphenylphosphoryl-2,3-dicyanonaphthalene, 0.75 g (2.56 mmol) of indium chloride tetrahydrate and 3 ml of quinoline was mixed at about 200 °C for about 6 hours and allowed to cool to about 60 °C, to which 60 ml of methanol was added and mixed for one hour to precipitate dark green solid. The solid was filtered and rinsed with methanol until the filtrate was transparent. It was then dispersed in 300 ml of a 3 % hydrochloric acid solution and mixed at 70 to 80 °C for about one hour. After filtering, it was rinsed with water and then rinsed with 300 ml of methanol, followed

45

by drying under reduced pressure to obtain 500 mg of solid. The solid was identified as tetrakis-(diphenylphosphoryl)chloroindiumnaphthalocyanine by the following analysis;

(1)

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Elemental analysis			
Calculated value (%)	C; 69.30,	H; 3.61,	N; 6.74
Measured value (%)	C; 67.64,	H; 3.82,	N; 6.41

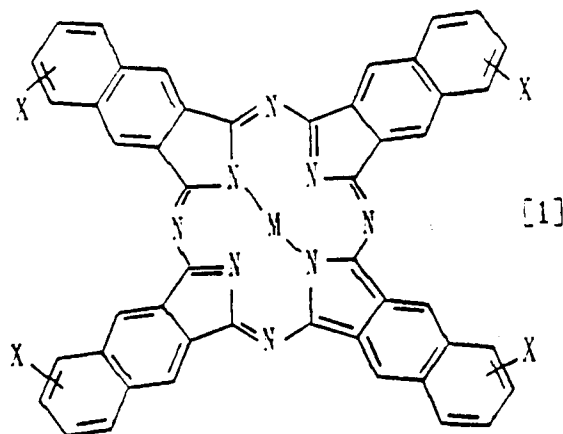
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(2) Electron spectrum in  $\text{CHCl}_3$  (Fig.16)

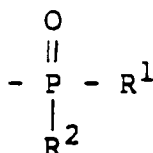
(3) IR spectrum (KBr method) (Fig.17)

## Claims

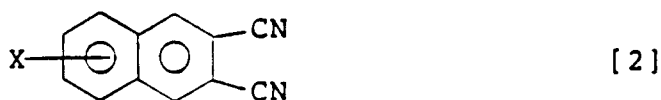
1. A naphthalocyanine compound which is represented by the following formula [1]



wherein X represents

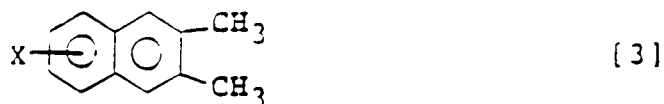


- (wherein R<sup>1</sup> and R<sup>2</sup> respectively represent a hydroxyl group, an alkyl group, an aryl group or an alkoxy group ) and M represents 2H, a metal atom, a metal oxide residue or a metal chloride residue.
2. An intermediate of the naphthalocyanine compound according to Claim 1, represented by the formula;

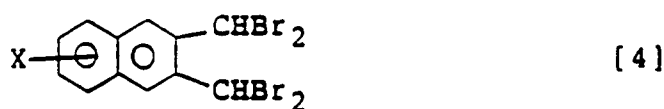


wherein X is the same as mentioned above.

3. A process for preparing the intermediate according to Claim 2, comprising;  
reacting 3- or 4-bromo-o-xylene with phosphine oxide or a phosphite to form a X substituted-o-xylene represented by formula [3]



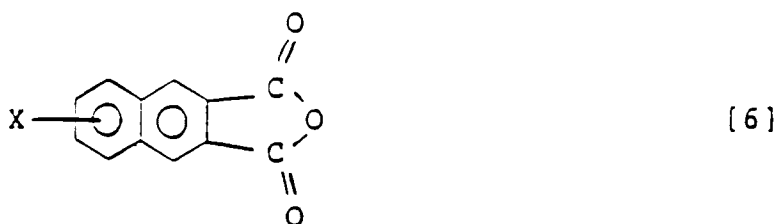
wherein X is the same as mentioned above,  
reacting it with N-bromosuccinimide to form a compound represented by formula [4]



wherein X is the same as mentioned above, and  
then reacting the compound [4] with fumaronitrile represented by formula [5]

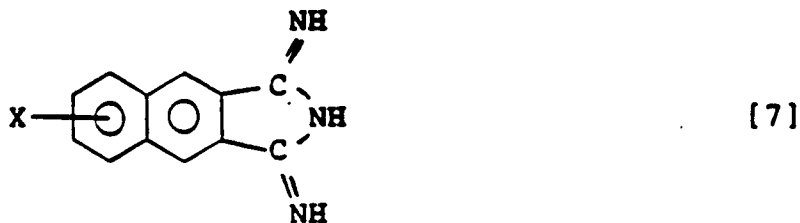


- 10
4. A process for preparing the naphthalocyanine compound [1] according to claim 1 wherein M represents 2H, comprising reacting the intermediate [2] of claim 2 in an alcohol in the presence of a proton transferring accelerator.
  - 15 5. A process for preparing the naphthalocyanine compound [1] according to claim 1 wherein M represents a metal atom, a metal oxide residue or a metal chloride residue, comprising reacting the intermediate [2] of Claim 2 with a metal, a metal oxide or a metal chloride under molten conditions or in a high boiling point solvent.
  - 20 6. A process for preparing the naphthalocyanine compound [1] according to claim 1 wherein M represents a metal atom, a metal oxide residue or a metal chloride residue, comprising reacting a X substituted naphthalene-2,3-dicarboxylic anhydride represented by formula [6]



wherein X is the same as mentioned above, with a metal, a metal oxide or a metal chloride under molten conditions or in a high boiling point solvent in the presence of urea.

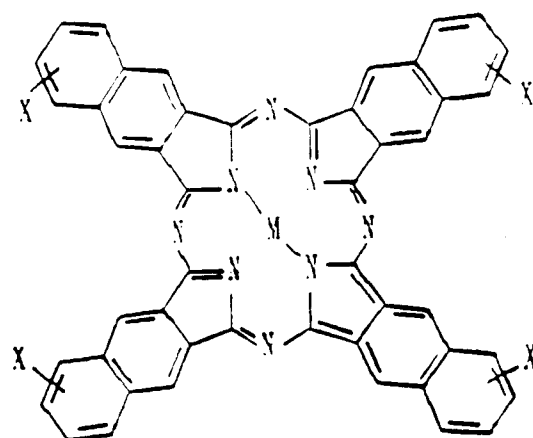
- 35
7. A process for preparing the naphthalocyanine compound [1] according to claim 1 wherein M represents a metal atom, a metal oxide residue or a metal chloride residue, comprising reacting a X substituted 1,3-diiminobenz (f) isoindoline represented by formula [7]
- 40



wherein X is the same as mentioned above, with a metal, a metal oxide or a metal chloride under molten conditions or in a high boiling point solvent in the presence of a tertiary amine.

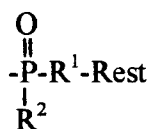
# Patentansprüche

1. Naphthalocyaninverbindung, welche durch die folgende Formel [1] wiedergegeben wird



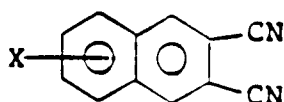
[1],

wobei X ein



ist (bei dem R<sup>1</sup> beziehungsweise R<sup>2</sup> eine Hydroxylgruppe, einen Alkyl-, einen Aryl- oder einen Alkoxyrest bedeuten) und M zwei Wasserstoffatome, ein Metallatom, einen Metalloxid- oder einen Metallchloridrest darstellt.

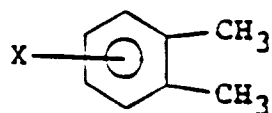
2. Zwischenstufe der Naphthalocyaninverbindung nach Anspruch 1, wiedergegeben durch die Formel [2]



[2],

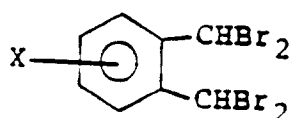
wobei X wie in Anspruch 1 beschrieben ist.

3. Verfahren zur Herstellung der Zwischenstufe nach Anspruch 2, umfassend Umsetzen von 3- oder 4-Brom-*ortho*-xylol mit Phosphinoxid oder einem Phosphit, um ein mit X substituiertes *ortho*-Xylol der Formel [3] zu bilden



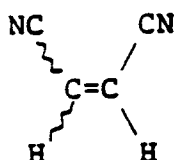
[3],

wobei X wie in Anspruch 1 beschrieben ist,  
Umsetzen mit N-Bromsuccinimid; um eine Verbindung der Formel [4] zu bilden



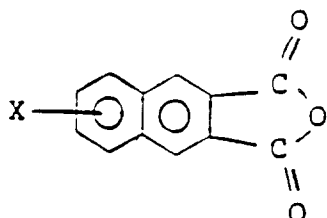
[4],

wobei X wie in Anspruch 1 beschrieben ist,  
und dann Umsetzen der Verbindung [4] mit Fumarnitril der Formel [5]



[5].

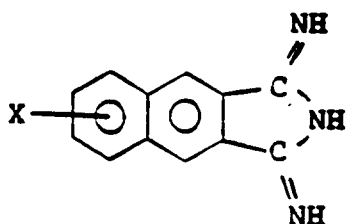
4. Verfahren zur Herstellung der Naphthalocyaninverbindung [1] nach Anspruch 1, wobei M zwei Wasserstoffatome bedeutet, umfassend Umsetzen der Zwischenstufe [2] aus Anspruch 2 in einem Alkohol in Gegenwart eines Protonenübertragungsbeschleunigers.
5. Verfahren zur Herstellung der Naphthalocyaninverbindung [1] nach Anspruch 1, wobei M ein Metallatom, einen Metalloxid- oder einen Metallchloridrest bedeutet, umfassend Umsetzen der Zwischenstufe [2] aus Anspruch 2 mit einem Metall, einem Metalloxid oder einem Metallchlorid unter Schmelzbedingungen oder in einem hochsiedenden Lösemittel.
6. Verfahren zur Herstellung der Naphthalocyaninverbindung [1] nach Anspruch 1, wobei M ein Metallatom, einen Metalloxid- oder einen Metallchloridrest bedeutet, umfassend Umsetzen eines mit X substituierten Naphthalin-2,3-dicarbonsäureanhydrids der Formel [6]



[6],

wobei X wie in Anspruch 1 beschrieben ist,  
mit einem Metall, einem Metalloxid oder einem Metallchlorid unter Schmelzbedingungen oder in einem hochsiedenden Lösemittel in Gegenwart von Harnstoff.

7. Verfahren zur Herstellung der Naphthalocyaninverbindung [1] nach Anspruch 1, wobei M ein Metallatom, einen Metalloxid- oder einen Metallchloridrest bedeutet, umfassend Umsetzen eines mit X substituierten 1,3-Diiminobenz(f)isoindolins der Formel [7]



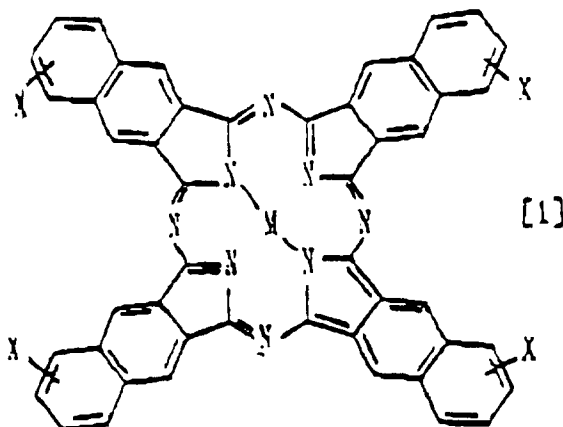
[7],

wobei X wie in Anspruch 1 beschrieben ist,

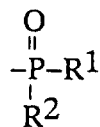
mit einem Metall, einem Metalloxid oder einem Metallchlorid unter Schmelzbedingungen oder in einem hochsiedenden Lösemittel in Gegenwart eines tertiären Amins.

# Revendications

1. Composé de naphthalocyanine qui est représenté par la formule [1] suivante :



dans laquelle X représente



(dans lequel R<sup>1</sup> et R<sup>2</sup> représentent respectivement un groupe hydroxyle, un groupe alkyle, un groupe aryle ou un groupe alcoxy) et M représente 2H, un atome métallique, un résidu d'oxyde métallique ou un résidu de chlorure métallique.

2. Intermédiaire du composé de naphthalocyanine selon la revendication 1, représenté par la formule :

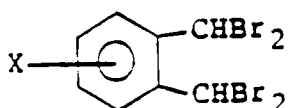


dans laquelle X est tel que défini dans la revendication 1.

3. Procédé pour la fabrication de l'intermédiaire selon la revendication 2, comprenant :  
la réaction du 3- ou 4-bromo-o-xylène avec l'oxyde de phosphine ou un phosphite pour former un o-xylène X-substitué représenté par la formule [3]

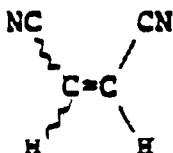


dans laquelle X est tel que défini dans la revendication 1,  
sa réaction avec le N-bromosuccinimide pour former un composé présenté par la formule [4]



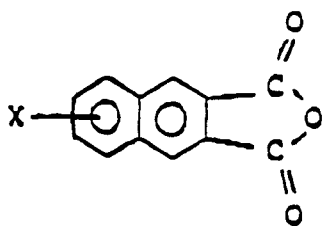
[ 4 ]

dans laquelle X est tel que défini dans la revendication 1 et  
ensuite la réaction du composé [4] avec le fumaronitrile représenté par la formule [5]



[ 5 ]

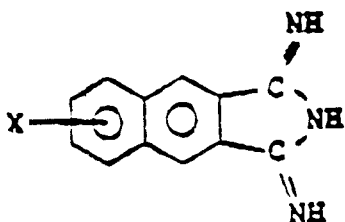
4. Procédé pour la fabrication du composé de naphtalocyanine [1] selon la revendication 1, dans lequel M représente 2H, comprenant la réaction de l'intermédiaire [2] selon la revendication 2 dans un alcool en présence d'un accélérateur de transfert de proton.
5. Procédé pour la fabrication du composé de naphtalocyanine selon la revendication 1, dans lequel M représente un atome métallique, un résidu d'oxyde métallique ou un résidu de chlorure métallique, comprenant la réaction de l'intermédiaire [2] selon la revendication 2 avec un métal, un oxyde métallique ou un chlorure métallique à l'état fondu ou dans un solvant de haut point d'ébullition.
6. Procédé pour la fabrication du composé de naphtalocyanine [1] selon la revendication 1, dans lequel M représente un atome métallique, un résidu d'oxyde métallique ou un résidu de chlorure métallique, comprenant la réaction d'un anhydride d'acide naphtalène-2,3-dicarboxylique X-substitué représenté par la formule [6]



[ 6 ]

dans laquelle X est tel que défini dans la revendication 1 avec un métal un oxyde métallique ou un chlorure métallique à l'état fondu ou dans un solvant de haut point d'ébullition en présence d'urée.

7. Procédé pour la fabrication du composé de naphtalocyanine [1] selon la revendication 1, dans lequel M représente un atome métallique, un résidu d'oxyde métallique ou un résidu de chlorure métallique, comprenant la réaction d'une 1,3-diiminobenzo(f)isoindoline X-substituée représentée par la formule [7]



[ 7 ]



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dans laquelle X est tel que défini dans la revendication 1. avec un métal, un oxyde métallique ou un chlorure métallique à l'état fondu ou dans un solvant de haut point d'ébullition en présence d'une amine tertiaire.

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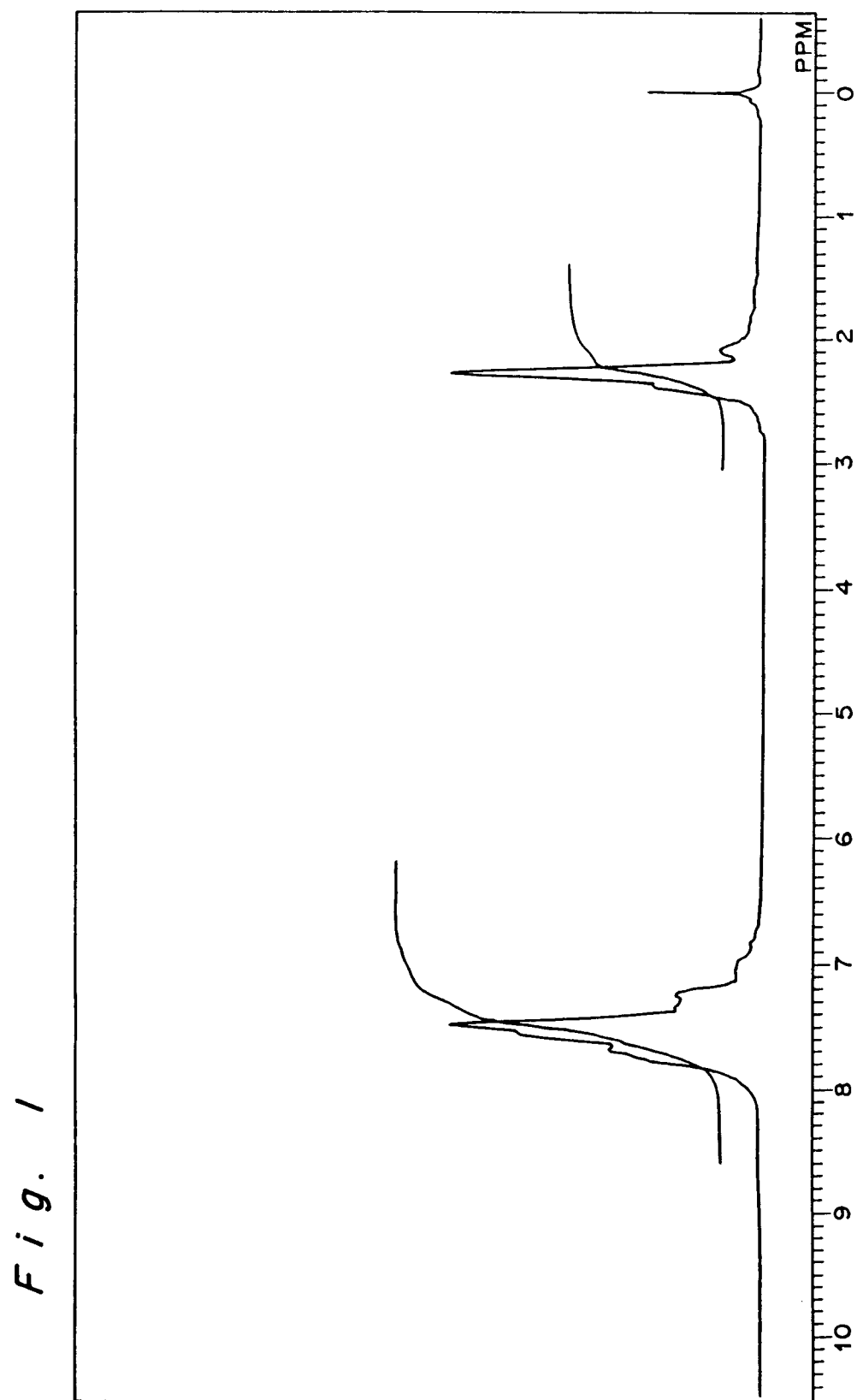


Fig. 2

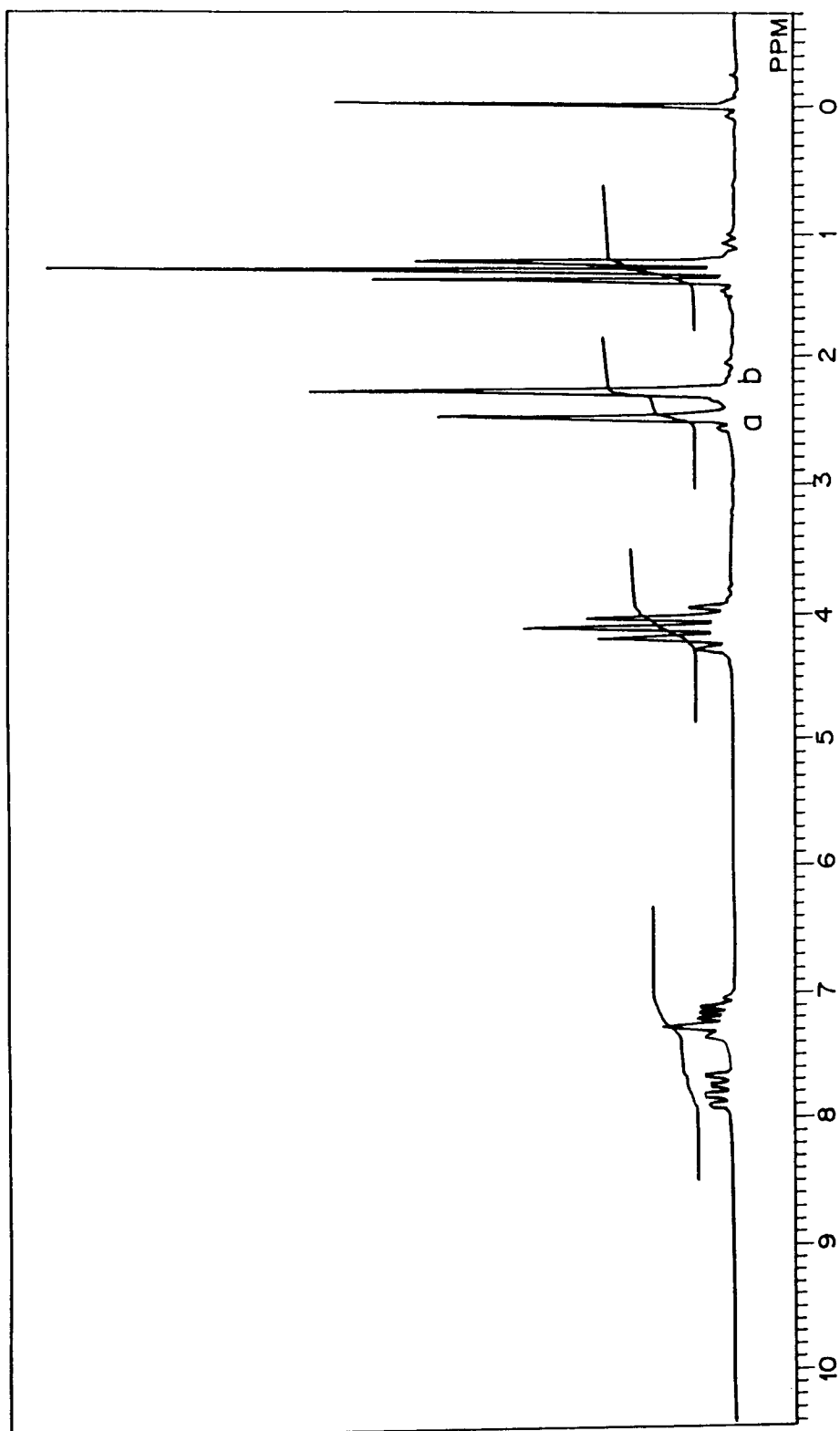
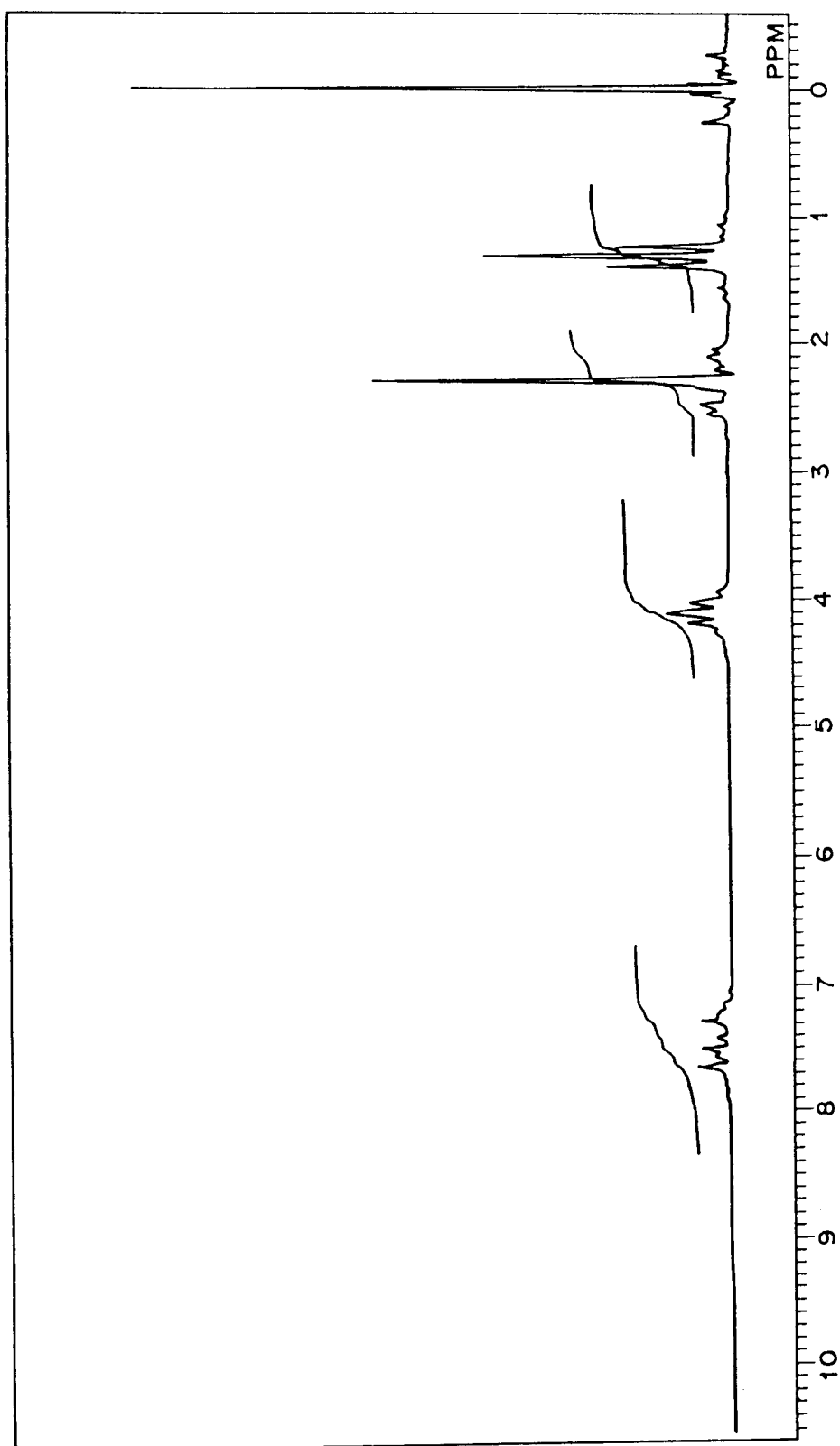
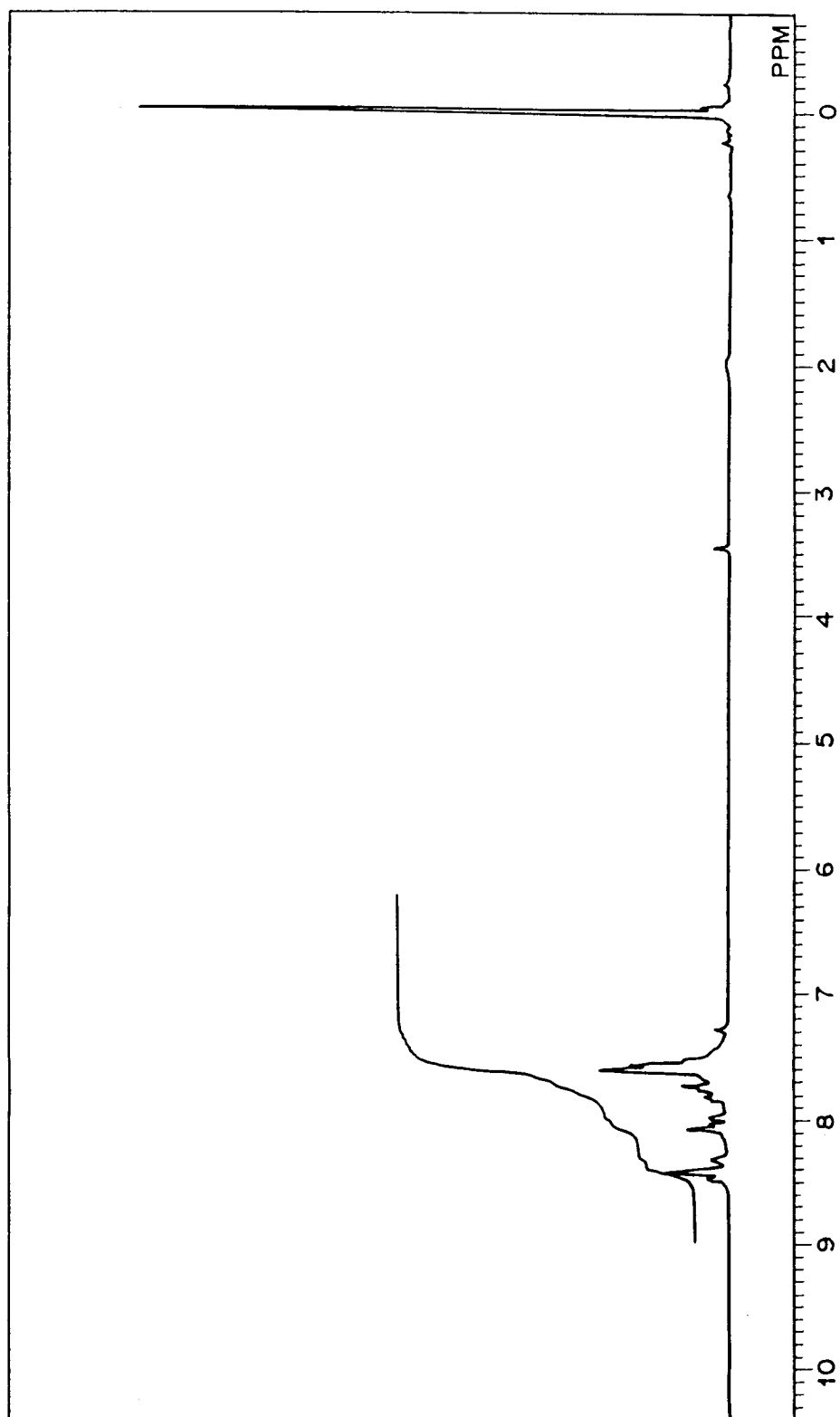
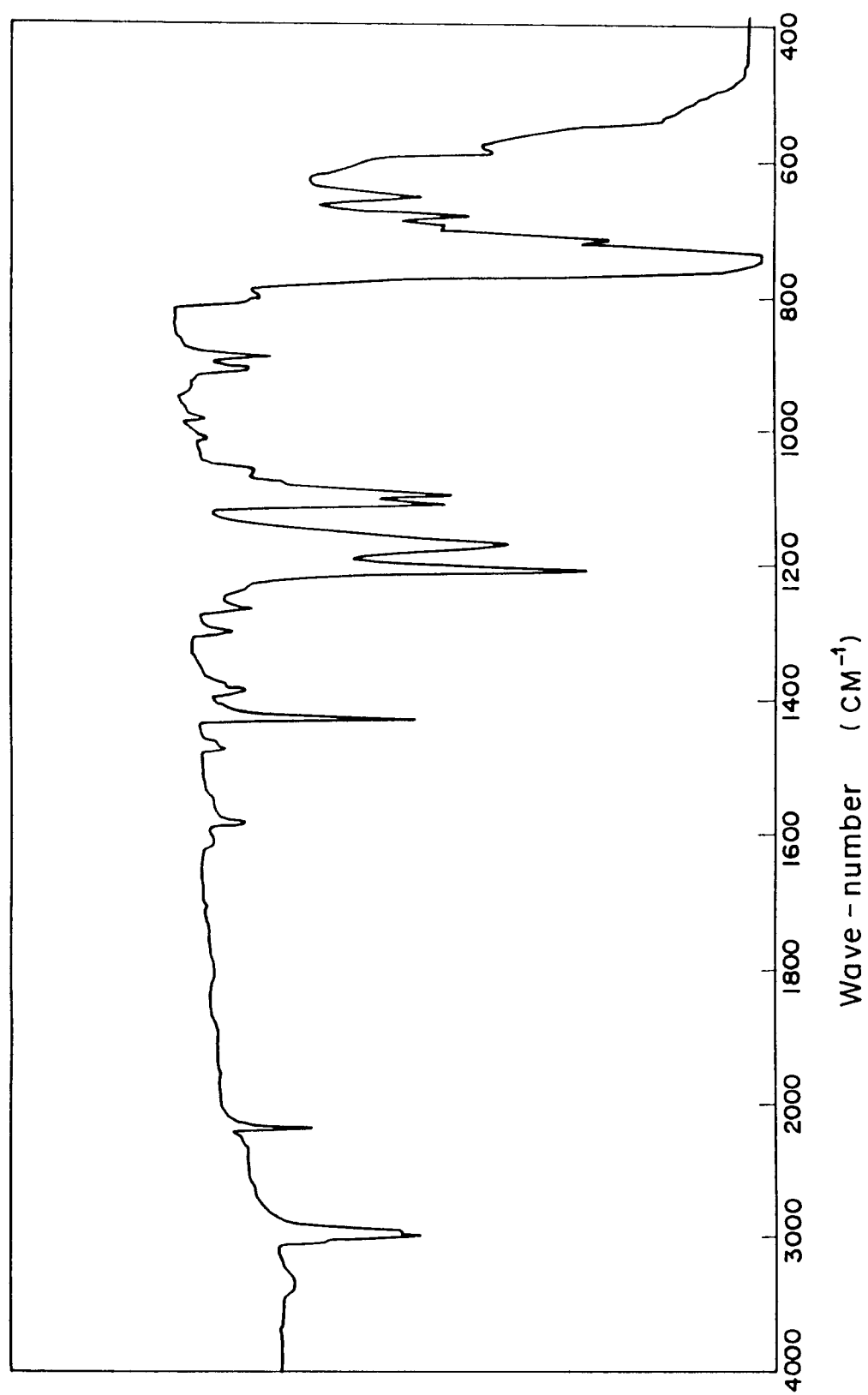


Fig. 3

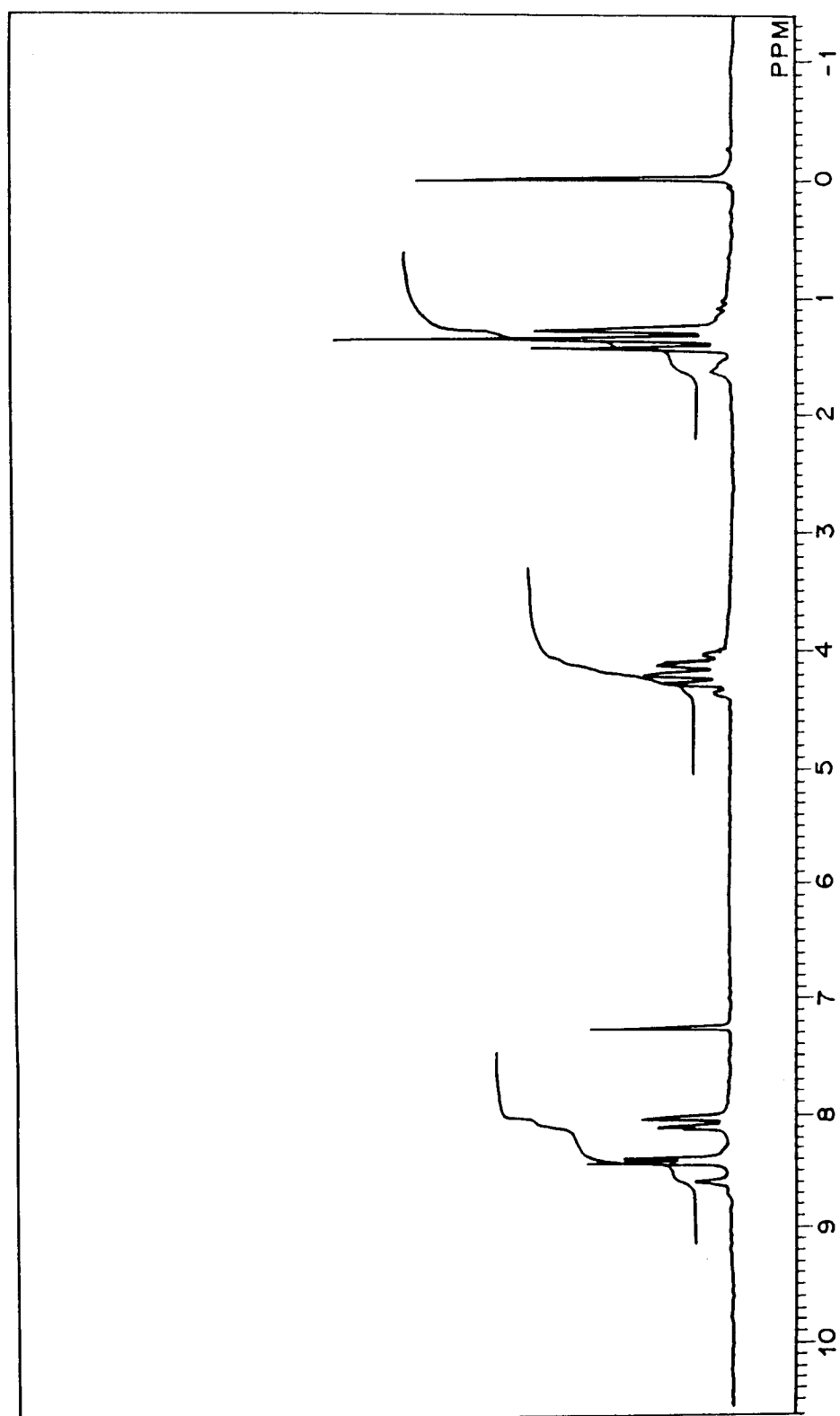


*Fig. 4*



*Fig. 5*

*Fig. 6*



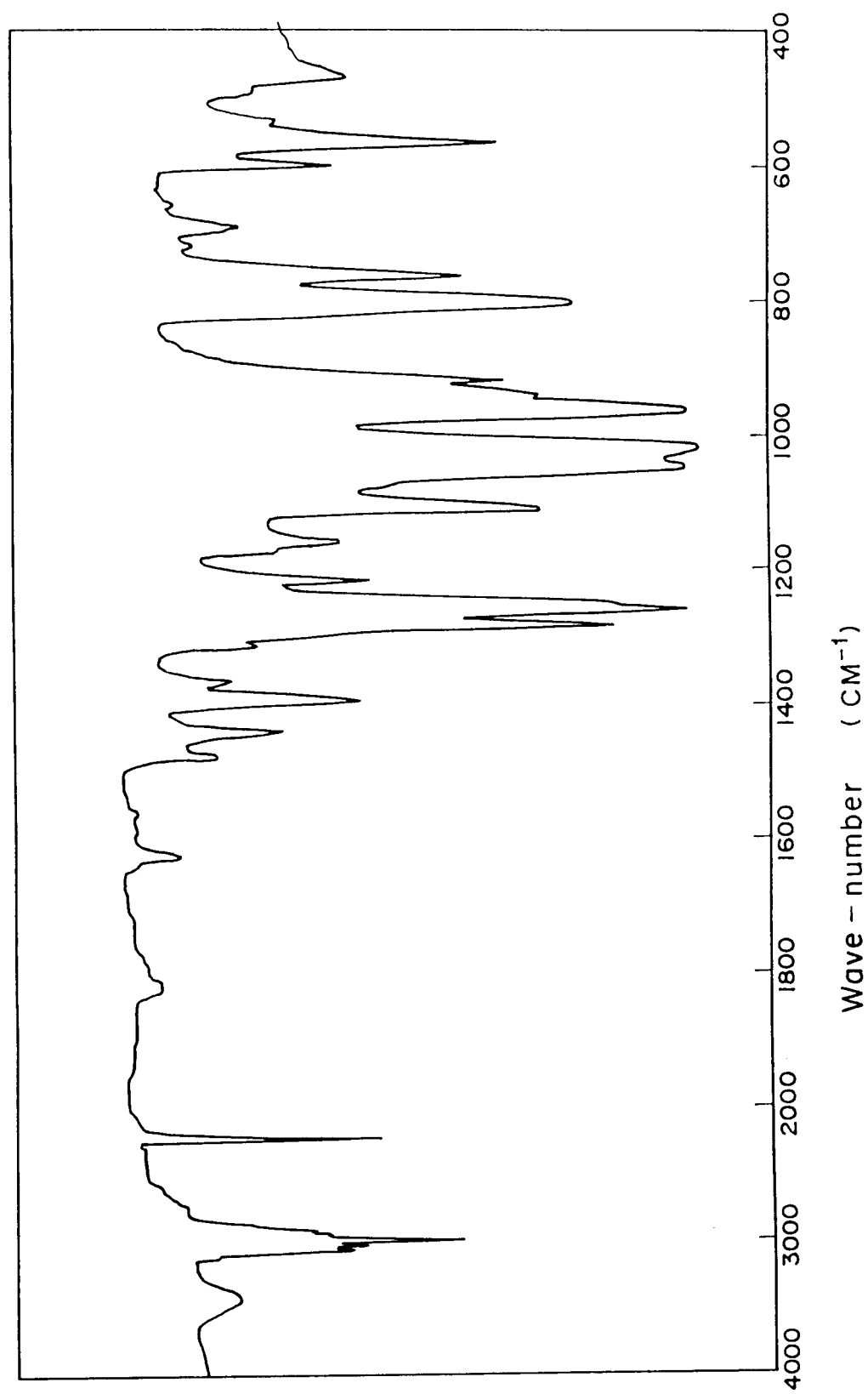
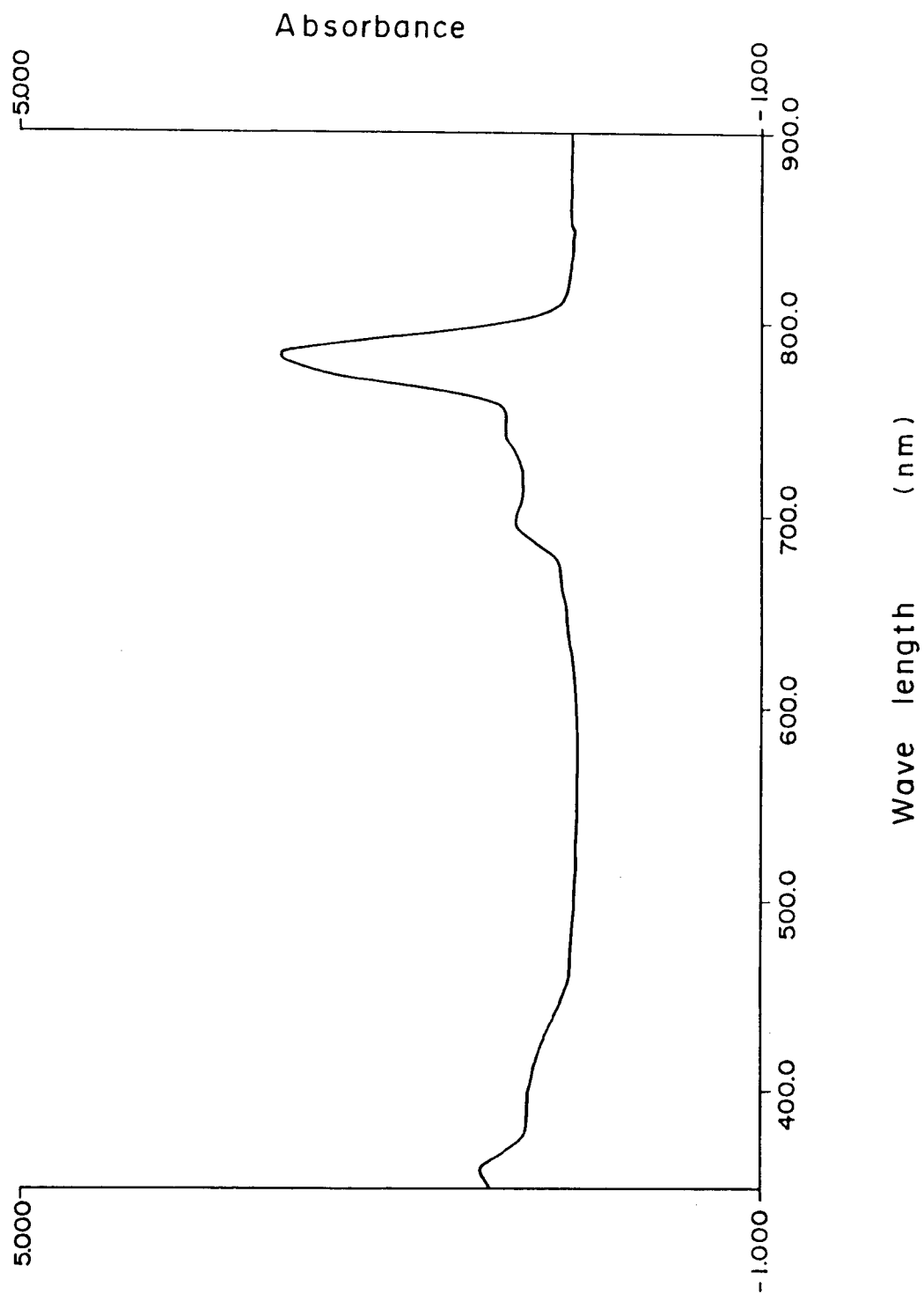
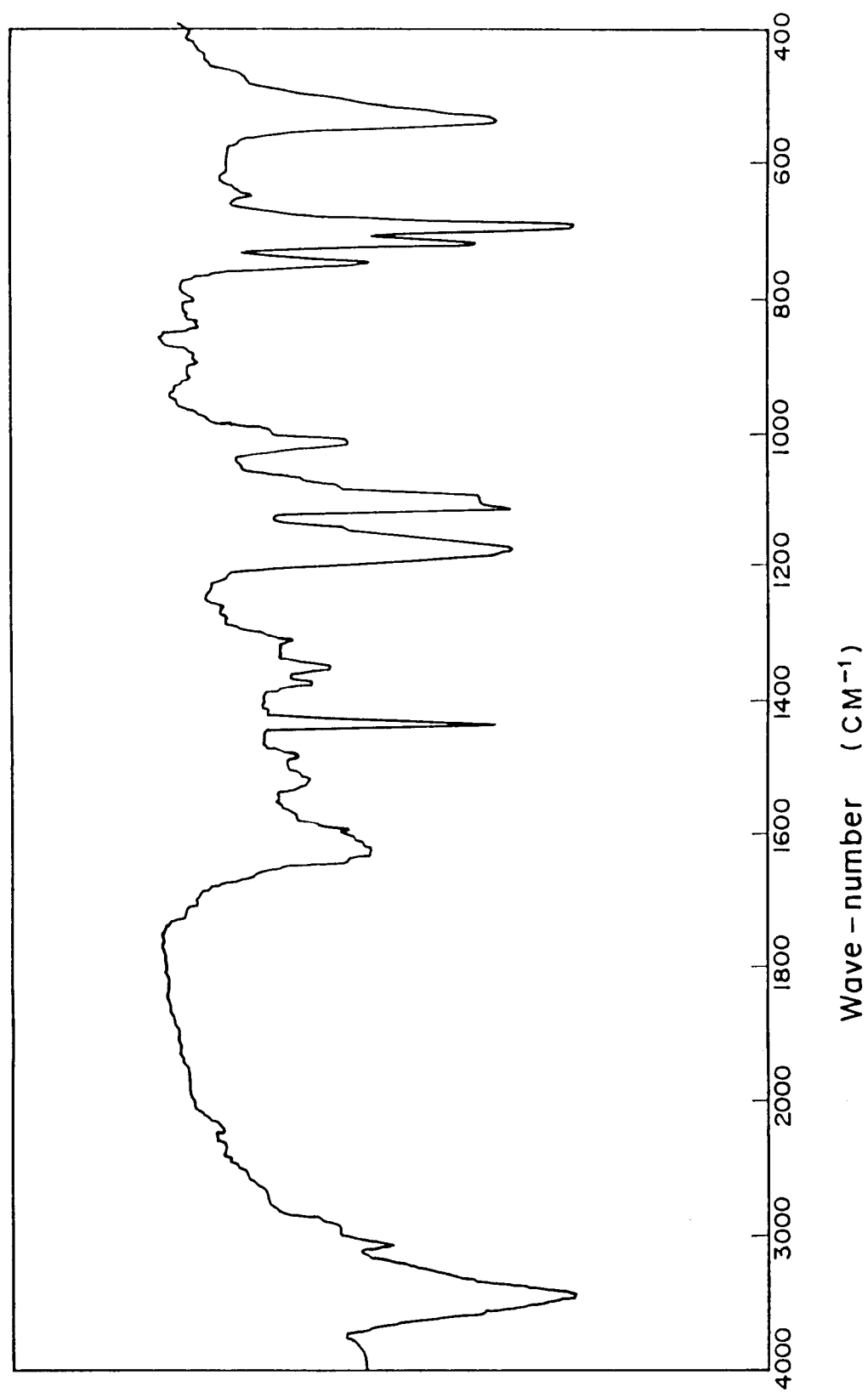
*Fig. 7*

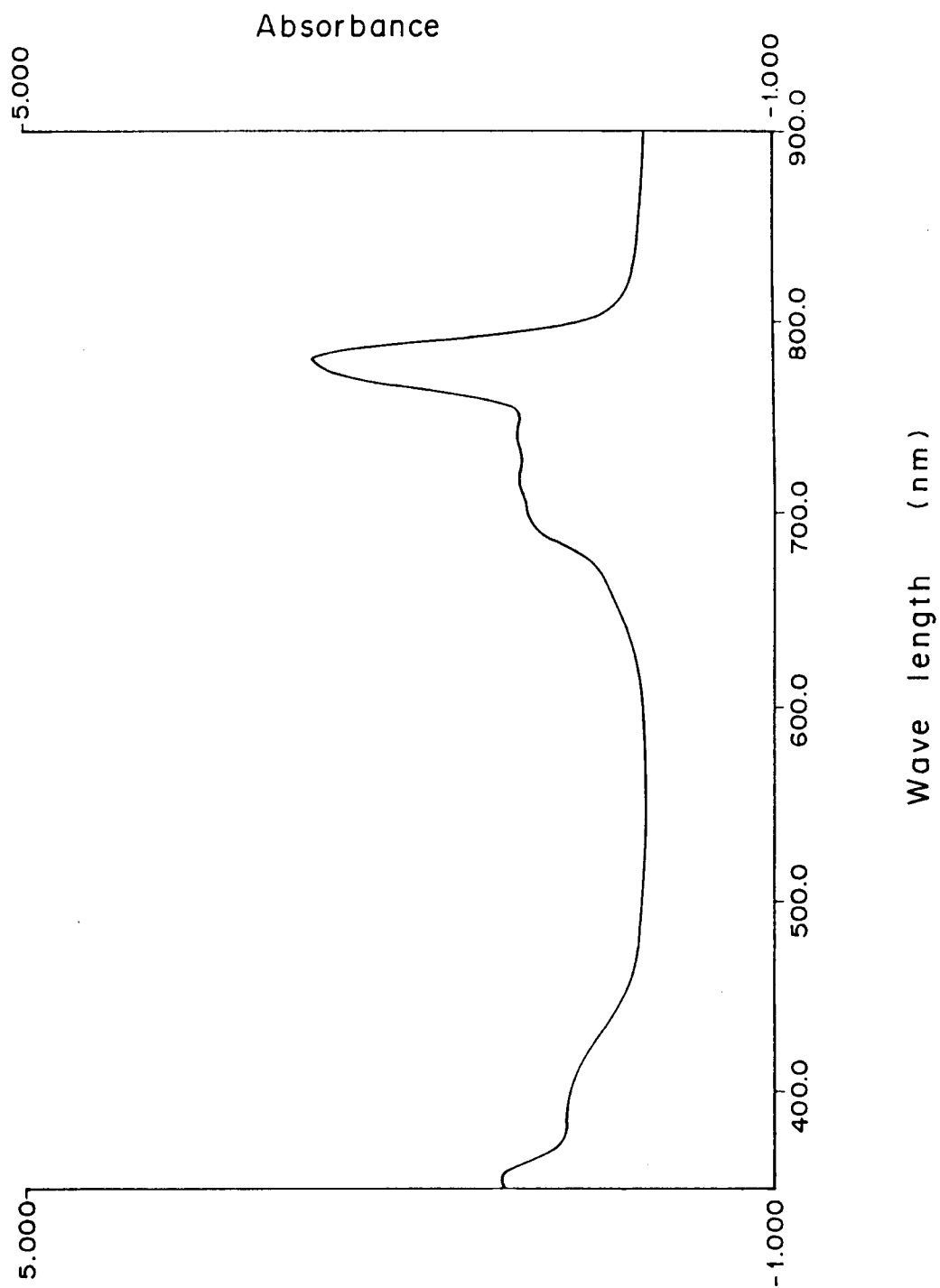


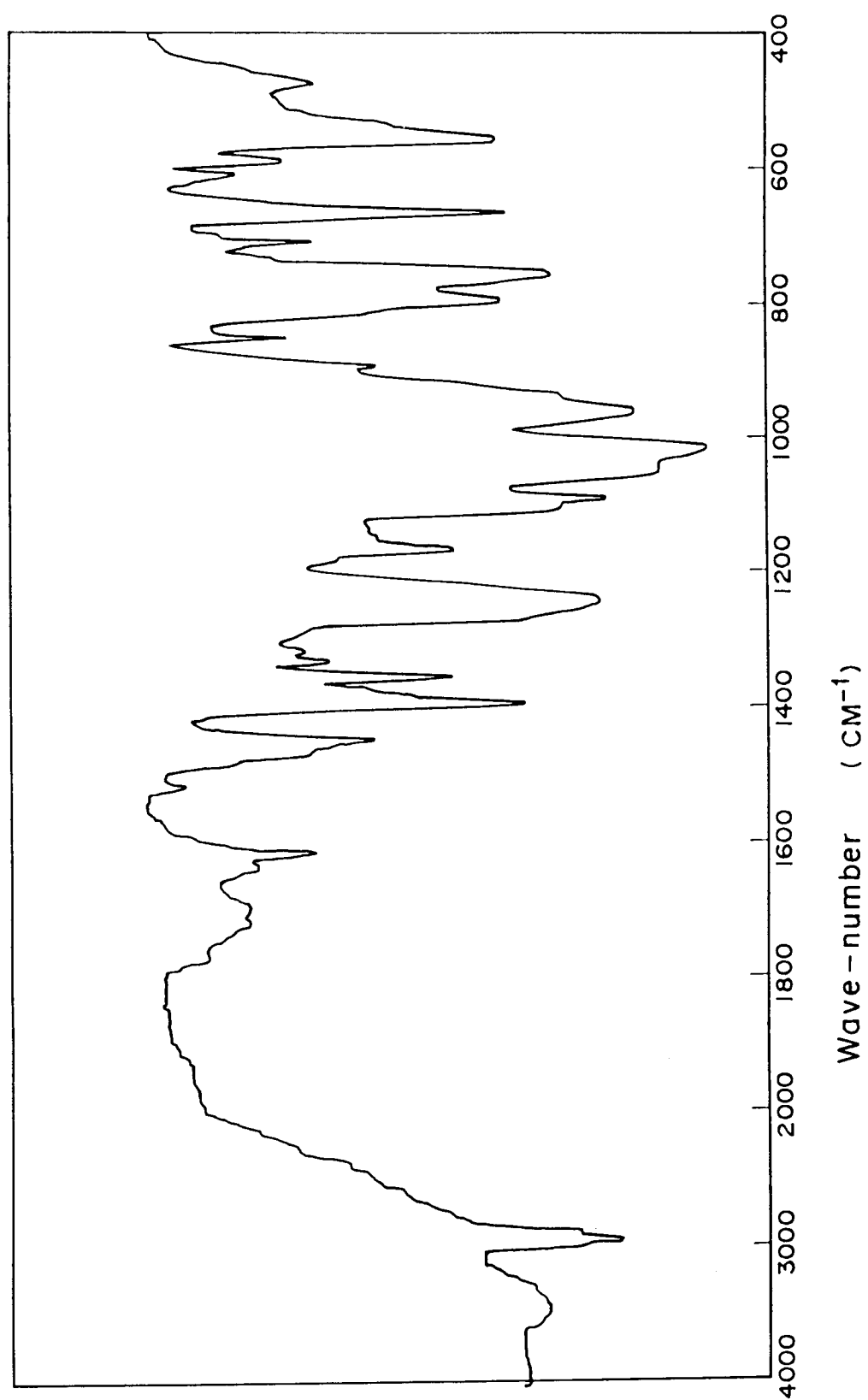
Fig. 8

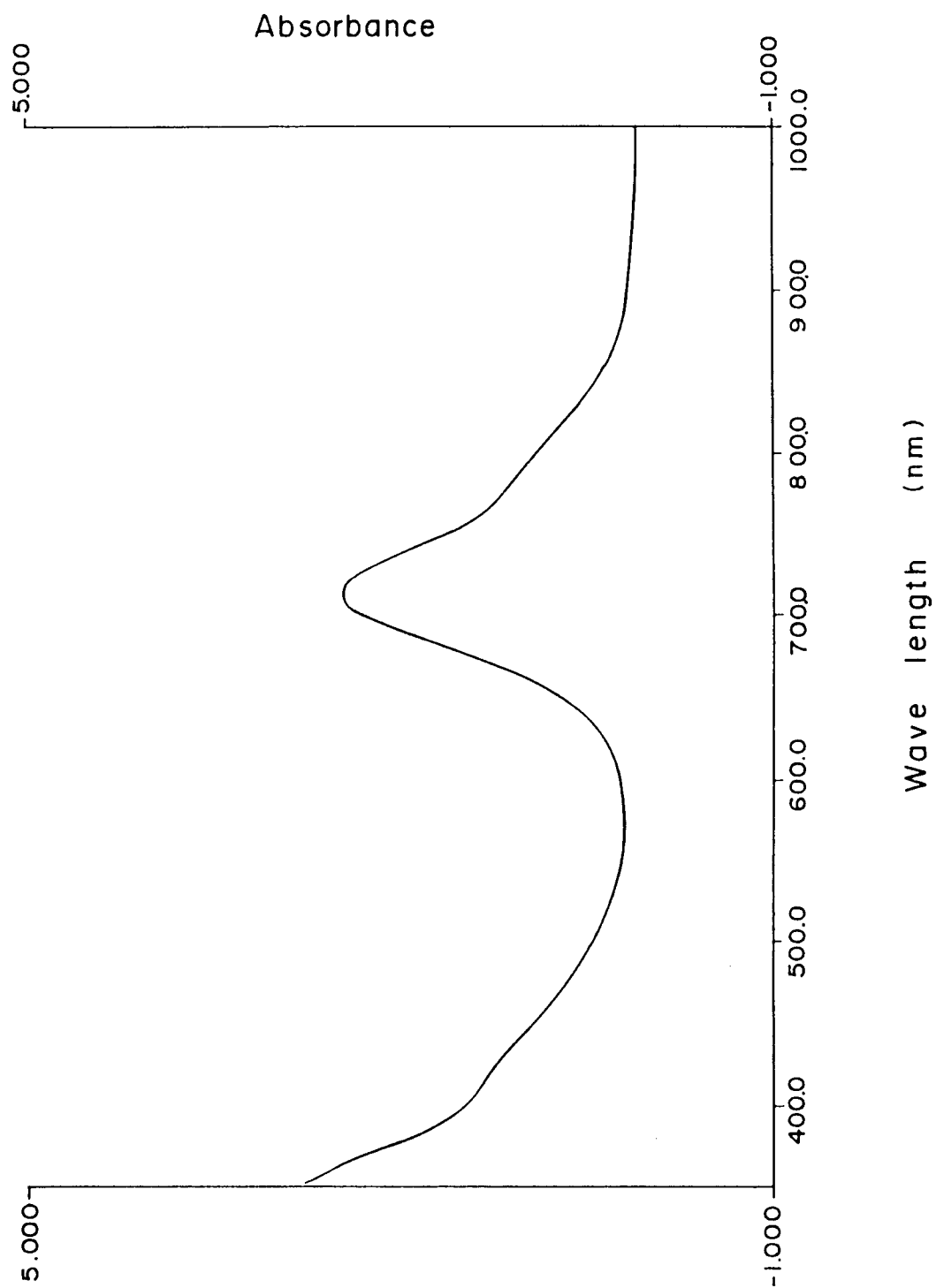


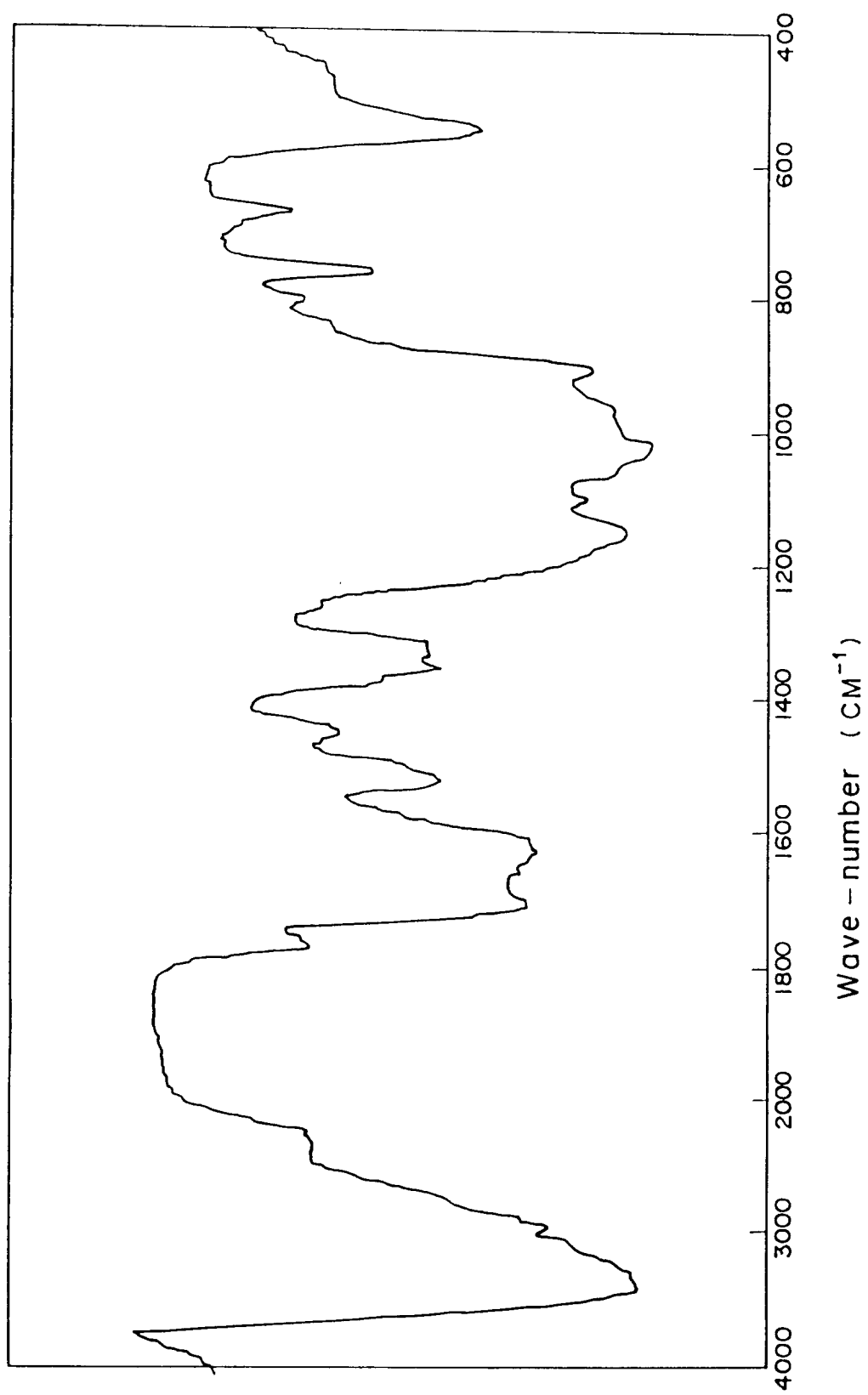
*Fig. 9*

*Fig. 10*

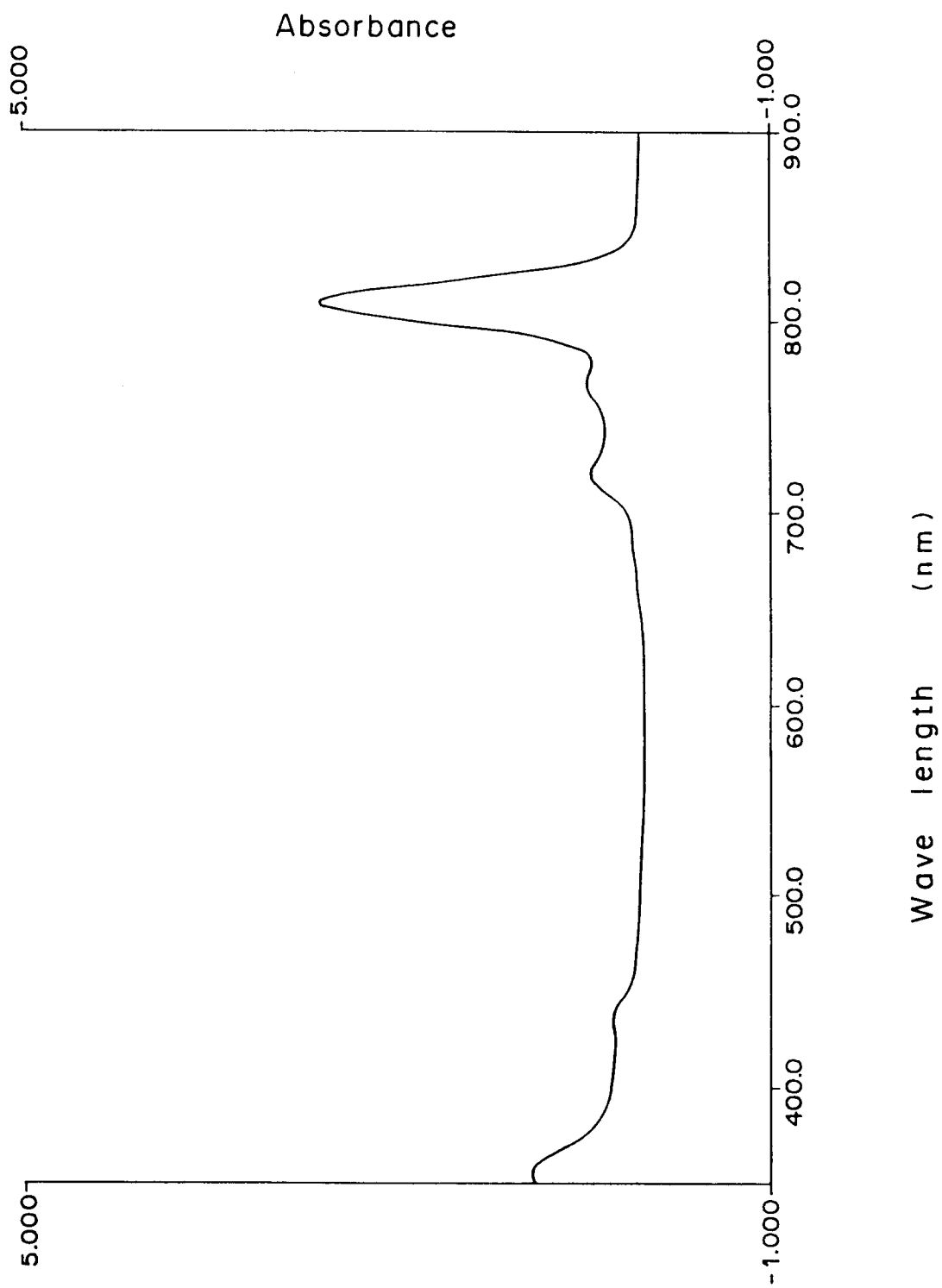


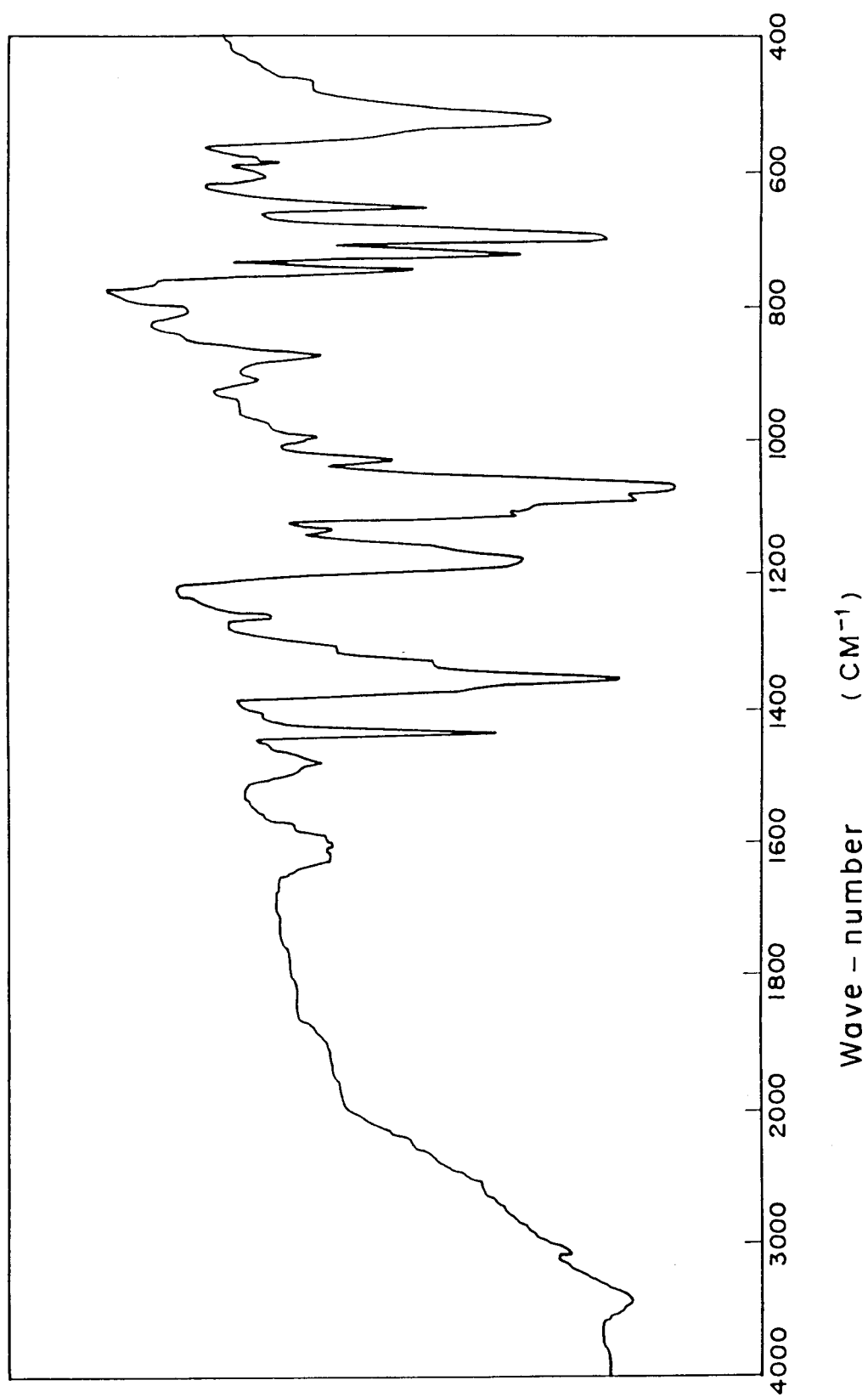
*Fig. 11*

*Fig. 12*

*Fig. 13*

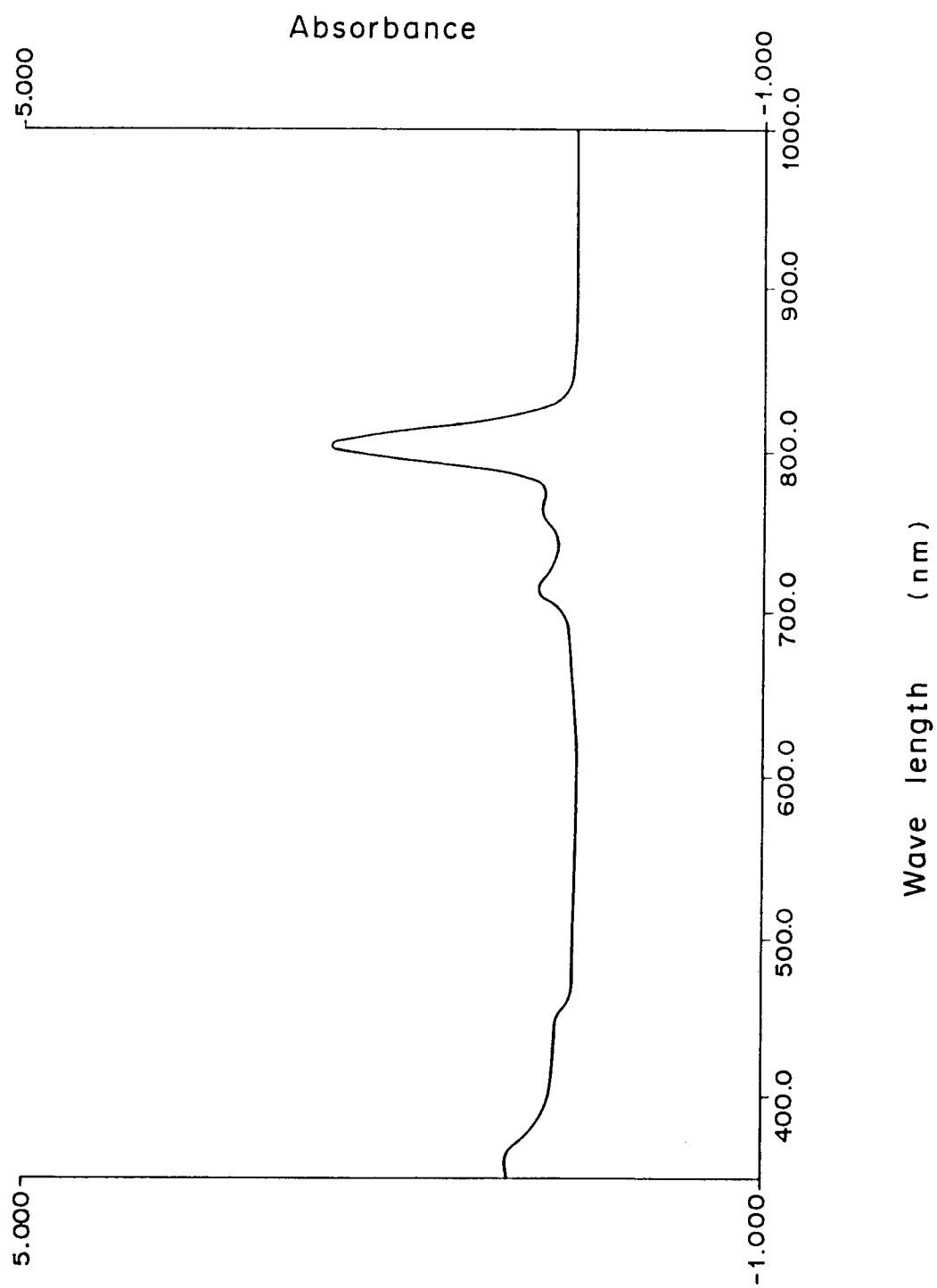
*Fig. 14*



*Fig. 15*



*Fig. 16*



*Fig. 17*